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Ferromagnetism of $CeSi_x$ at ambient and high pressure

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We have made detailed investigations of the structural and magnetic properties of $CeSi_x$ ($1.0 \le x \le 2.0$). The homogeneity region of the $ThSi_2$-type ($GdSi_2$-type) $CeSi_x$ phase is limited to the Si concentrations x: $1.67 \le x \le 2.0$ and does not extend to the concentration range $1.55 \le x \le 2.0$, as was reported previously. A transformation from the tetragonal $ThSi_2$-type structure to the orthorhombic $GdSi_2$-type structure appears to occur in the $CeSi_x$ system in the same range ($1.84 < x < 1.9$) where ferromagnetism appears and the specific-heat coefficient γ passes through a peak. The presence of an unknown stable phase with composition intermediate to $CeSi_{1.0}$ and Ce_3Si_5 has been detected. Magnetically ordered ground states have been observed for $x \le 1.84$ and no magnetic or superconducting ordering above 400 mK has been detected for $x \ge 1.90$. The present data indicates that magnetism in the $CeSi_x$ system may not be simple ferromagnetic. The experimental behavior of this system appears to be Kondo-lattice-like both at ambient and high pressure.

I. INTRODUCTION

Ce in its compounds and alloys exists either in a nearly trivalent state or in a fractional (intermediate) valence state. For the last two decades the physics of fractional-valence Ce systems has been of considerable interest and is well documented.[1–5] Nearly trivalent Ce systems, however, remained of secondary interest until the discovery of heavy-fermion superconductivity in a nearly trivalent Ce compound $CeCu_2Si_2$ is 1979.[6] Since then, the search for heavy-fermion systems (those with large effective electron mass and giant values of the specific-heat coefficient γ) has diverted considerable attention to nearly trivalent Ce systems.

In nearly trivalent Ce systems, the single magnetic $4f$ electron localized below the Fermi level and hybridizing with the conduction electrons bears resemblance with virtual bound-state formation in the single-impurity Friedel-Anderson-Kondo problem. However, one essential difference is that the Ce "impurity" in compounds is not noninteracting. Magnetic $4f$ electrons interact with one another via conduction electrons (s-f exchange interaction) and may lead to a magnetically ordered ground state by the Ruderman-Kittel-Kasuya-Yosida (RKKY) mechanism.[1] On the other hand, $4f$ conduction-electron interaction may also lead to a compensation of the $4f$ magnetic moment via the Kondo mechanism, as is the case in the single-impurity problem. These two competing mechanisms are operative in almost all nearly trivalent Ce systems. For that reason nearly trivalent Ce systems are often referred to as Kondo-lattice systems or condensed Kondo systems.[7] The physical properties of such systems are determined by the relative strength of the RKKY and Kondo interactions. If the RKKY energy $W_{\mathrm{RKKY}} \sim CJ^2N(0)$ is appreciably higher than the Kondo energy $W_K \sim N^{-1}(0)\exp[1/N(0)|J|]$ the ground state is magnetically ordered (e.g., $CeIn_3$, CeZn, etc.) and if $W_K > W_{\mathrm{RKKY}}$ then the ground state is essentially nonmagnetic (e.g., $CeAl_3$ and $CeSn_3$).[8] C is a constant, $N(0)$ is the density of the states at the Fermi level, and J is the exchange constant.

As far as heavy-fermion behavior is concerned a giant γ indicates a high density of states at the Fermi level and the large effective (electron) mass hints at the existence of a narrow band. All known heavy-fermion Ce compounds also appear to be bonafide Kondo-lattice systems. Therefore, it would be very useful to know the range of W_K which is suitable for heavy-fermion behavior. It is probably a resonancelike situation of the hybridization between the f states and the conduction-band states during which the above-mentioned conditions for the heavy-fermion behavior are met. However, the narrow energy range in which this resonancelike situation exists seems to be very rarely accessible in physical systems: this is apparent from the fact that only very few heavy-fermion systems are known. The energy range of interest for heavy-fermion behavior which appears to be very narrow must be compatible with all three types of magnetic, nonmagnetic, and superconducting ground states: as all three types of ground states have been observed in heavy-fermion systems. In these respects, $W_K \approx W_{\mathrm{RKKY}}$ seems to be the only narrow energy range which would be consistent with all three types of ground states. Whether this energy range is suitable for the discovery of new heavy-fermion systems must await further experimentation. $CeSi_x$ is a promising system in this respect, as the energy range of interest is physically accessible in this system.

An important parameter which governs the systematics of Kondo-lattice systems is the magnitude of the exchange constant $|J|$. J can be varied either by alloying or by external pressure. External pressure has the advantage that it is free from any complications which may arise from local environmental effects. We have used both techniques to study the properties of the Kondo-lattice system $CeSi_x$. We discuss the results in the light of theoretical predictions for the Kondo-lattice state.[7,8]

The existence of the compound $CeSi_2$, which crystallizes in the $ThSi_2$ type structure was reported as early as 1865.[9] A broad homogeneity region for the tetragonal $CeSi_2$ phase with decreasing Si concentration (e.g., $CeSi_x$, $1.78<x<2.00$) and high temperature (77–500 K) magnetic susceptibility data were reported in 1964.[10] Later, $CeSi_2$ became the object of numerous investigations in the context of intermediate valency and Kondo phenomena.[11–15] L_{III}-edge x-ray absorption and x-ray photoemission studies revealed a nearly trivalent state of Ce (valence <3.02) in this compound.[11,14,15] On the other hand, no signs of magnetic ordering were detected above 100 mK.[16] Above 200 K Curie-Weiss behavior is observed; the magnetic susceptibility becomes independent of temperature ~ 100 K, rising again at low temperature.[12] At low temperature a T^2 dependence in the magnetic susceptibility has been reported,[16] pointing to Fermi-liquid behavior in this system. In these respects this system resembles $CeSn_3$ and $CeAl_3$. However, unlike $CeSn_3$ no maxima in the susceptibility is observed and the specific-heat coefficient γ of $CeSi_2$, though moderately high in magnitude (104 mJ/mole K),[17] is an order of magnitude lower than that of $CeAl_3$, which originates from the heavy-fermion behavior in the latter compound.[18]

Interest for the study of the $CeSi_x$ system increased when Yashima *et al.*[16] reported an extended homogeneity region ($1.55 \le x \le 2.0$) and a magnetic-nonmagnetic transition as a function of the Si concentration; $CeSi_x$ undergoes a ferromagnetic transition ($T_c < 11$ K) for $x \le 1.80$ and remains paramagnetic down to 100 mK for $x \ge 1.90$. In a subsequent paper[17] they verified the tendency of this system towards heavy-fermion behavior by demonstrating the diverging nature of γ in the region of the magnetic-nonmagnetic boundary ($1.80<x<1.85$). We have made detailed structural and magnetic studies of $CeSi_x$ ($1.0 \le x \le 2.0$) at both ambient and high pressure to further explore the physics of this interesting system.

II. EXPERIMENT

The samples were prepared on a water-cooled Cu crucible in an induction furnace using commercial Ce (99.9%, Kurt Rasmus and Co.) and Si (99.999%, Wacker Chemitronics). In an attempt to prepare the samples in vacuum $\sim 10^{-5}$ Torr, weight losses were typically 1%. Therefore, samples were melted in a high-purity Ar (99.995%) atmosphere at 1.3 bar. The samples of mass ~ 1 g were turned over and remelted six times to ensure homogeneity. The weight losses in this process were $<0.1\%$ in all cases. Half of each sample was wrapped in a Ta foil sealed in a quartz tube under high vacuum and annealed at 1250 K for three days.

X-ray powder patterns were obtained for as-cast samples as well as for annealed samples with a Guinier camera using Co $K\alpha$ radiation and an internal Si standard. For as-cast samples, x-ray powder patterns with a diffractometer were also obtained. The sharpness of the x-ray pattern is nearly the same for as-cast and annealed samples.

For magnetization and magnetic susceptibility measurements the standard Faraday method was used. For ambient-pressure measurements, the sample was placed in a 5-g ultrapure Co crucible which was supported in the center of a large superconducting solenoid which was normally operated with a main field of 57 kOe and gradient field of 640 Oe/cm. The coils of this magnet were specially wound so that the product HdH/dz is constant to better than 1% over a cylinder of 2 cm in diameter and 5 cm in height, thus obviating the necessity of maintaining a precisely constant position for the pressure clamp or crucible with respect to the magnet as the temperature was varied.

High pressures were generated within the 5-mm diameter bore of a 90-g pressure clamp of standard design[19] made of pure binary Cu-Be with Al_2O_3 anvils. The hydrostatic pressure cell consisted of a thin-walled Delrin tube with Cu-Be end stoppers filled with a 1:1 Isoamyl-Isopentanc pressure fluid. A tiny Pb superconducting manometer[20] was also included in the cell. Upon cooling from 300 to 3 K the pressure decreased by 2–3 kbar.

The present temperature and pressure range of the apparatus are 2.5–300 K and 0–20 kbar, respectively. The temperature of the sample is determined using a calibrated carbon-glass thermometer located only a few millimeters away from the pressure clamp. The sample tube is filled at 300 K with 1-Torr He exchange gas. Further details of the experimental apparatus are given in Ref. 21.

III. RESULTS OF THE EXPERIMENT

For structural and magnetic studies across the $CeSi_x$ series the following Si concentrations were selected: $x=1.0$, 1.5, 1.6, 1.67, 1.70, 1.75, 1.80, 1.84, 1.90, 2.0. The results are presented in the following subsections.

A. Structural studies

Our structural analysis shows that for the $x \ge 1.67$ the anticipated tetragonal symmetry of the $ThSi_2$-type structure is retained with the possibility of a transformation to an orthorhombic $GdSi_2$-type structure for low Si concentrations ($x \le 1.84$) and with no traces of any secondary phase apparent either in the as-cast or in the annealed state. In the $CeSi_{1.5}$ and $CeSi_{1.6}$ samples, in addition to the anticipated $GdSi_2$-type orthorhombic phase, $\sim 8\%$ of $CeSi_{1.0}$ phase is present in the as-cast state; in the annealed state another unidentified impurity phase is found.[22] The above x-ray results are supported by metallographic studies in which clean polished surfaces of the samples were examined under a microscope using monochromatic Na light. No traces of any secondary phase, big grains, and clean grain boundaries were typical features for the samples with Si concentration $x > 1.67$. Traces ($<1\%$) of a secondary phase(s) were apparent at the grain boundaries in the $CeSi_{1.67}$ sample. In $CeSi_{1.5}$ and $CeSi_{1.6}$ samples, a secondary phase was apparent with different grain structures in the as-cast and annealed state, indicating the different nature of the secondary phase in

TABLE I. Structural and magnetic data for as-cast $CeSi_x$. Ordering temperature T_c was determined on annealed samples using static magnetization (left) and ac susceptibility (Right) techniques.

Sample	Lattice parameters a (Å)	b (Å)	c (Å)	Volume (Å)^3	Curie constant $\frac{\text{emu K}}{\text{mole Ce}}$	Θ (K)	M_{eff} $\frac{\mu_B}{\text{Ce atom}}$	T_c (K)	
$CeSi_{2.00}$	4.191		13.949	245.0	0.942	−249	2.74		
$CeSi_{1.90}$	4.189		13.893	244.5	0.832	−134	2.58		
$CeSi_{1.84}$	4.183		13.860	242.6	0.729	−52	2.44	6.7	5.8
$CeSi_{1.80}$	4.178		13.850	241.6	0.730	−37	2.42	10.6	10.0
$CeSi_{1.75}$	4.168		13.850	240.6	0.727	−27	2.41	11.0	10.4
$CeSi_{1.70}$	4.190	4.135	13.872	240.3	0.751	−23	2.45	12.9	12.1
$CeSi_{1.67}$	4.188	4.118	13.880	239.4	0.707	−12	2.38	13.2	12.4
$CeSi_{1.60}$	4.190	4.125	13.880	239.9	0.750	−8	2.45	12.0	11.4
$CeSi_{1.50}$	4.189	4.123	13.875	239.6	0.728	−13	2.41	12.0	11.3

the as-cast and annealed state, in agreement with x-ray results.

The lattice-parameter results presented in Table I are derived from x-ray powder data on as-cast samples and are in good agreement with previous data.[10,17] In Fig. 1 we display the variation of the lattice parameters a,b,c and of the unit-cell volume as a function of Si concentration x across the $CeSi_x$ series. The unit-cell volume shows a slow linear decrease with decreasing Si-concentration x. In fact, the decrease in the unit cell volume is only $\sim 0.12\%$ for a 1% decrease in x. In the multiphased regime ($x<1.67$) the unit-cell volume and lattice parameters remain nearly constant. The homogeneity range for the $CeSi_x$ phase is clearly limited to the Si concentrations $1.67 \le x \le 2.0$.

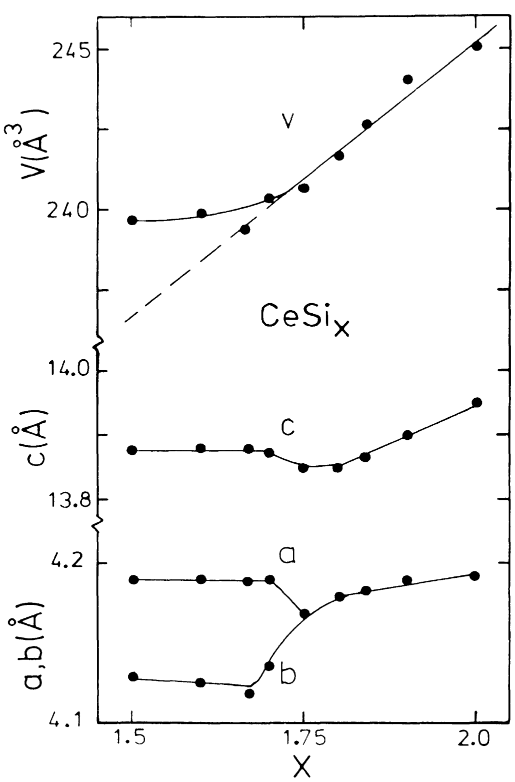

FIG. 1. Variation of the lattice parameters a,b,c and unit-cell volume V across the $CeSi_x$ series. Solid lines through data are guide to eye. Dotted line is linear extrapolation.

Another interesting observation is that some orthorhombic distortion due to the transformation from $ThSi_2$-type (tetragonal) to GdSi-type (orthorhombic) structure seems to appear in a concentration region near $x=1.84$ where the magnetic-nonmagnetic boundary lies. The transformations from the $ThSi_2$-type to the $GdSi_2$-type structure are very common among RSi_2(R=rare earth) compounds. Perri *et al.*,[23] who studied these transformations in RSi_2 compounds as a function of temperature, report that in several cases the transformation temperatures could not be determined precisely as the transformations were incomplete over broad temperature regions. In their investigations, they had used the splitting of the (200) lines as an indicator of the orthorhombic/tetragonal transformation. In our x-ray spectra at 295 K across the $CeSi_x$ series a weak splitting of the (200)-line is also apparent for $x \le 1.84$. Although the possibility exists that the diffuse nature of the (200) line may be a consequence of the broad homogeneity region of the tetragonal $CeSi_x$ phase, various observations[21] support the interpretation of the splitting of (200) line for the initiation of a orthorhombic transformation in this system. For $1.75 \le x \le 1.84$ the transformation is incomplete at 295 K and probably completes at a lower temperature. Whereas, for $x \le 1.7$ the transformation is complete at 295 K (for details see Ref. 21).

B. Magnetization studies

1. Ambient pressure

In Fig. 2 the inverse of the static magnetic susceptibility of as-cast $CeSi_x$ samples in the temperature range 2.6–300 K is displayed. The Curie-Weiss behavior is limited to temperatures above 200 K in case of $CeSi_{2.0}$, in

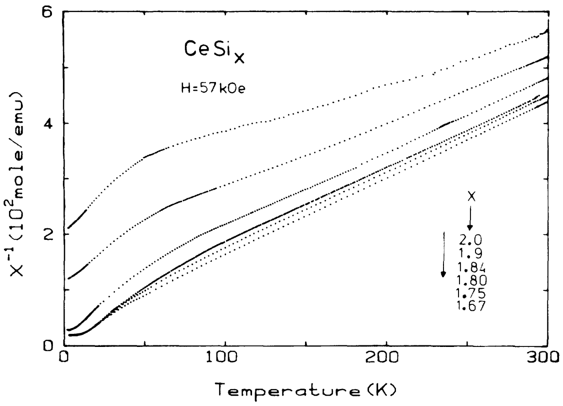

FIG. 2. Inverse of the magnetic susceptibility of CeSi$_x$ as a function of temperature. Si concentration for the uppermost curve is $x=2$ and decreases from top to bottom systematically.

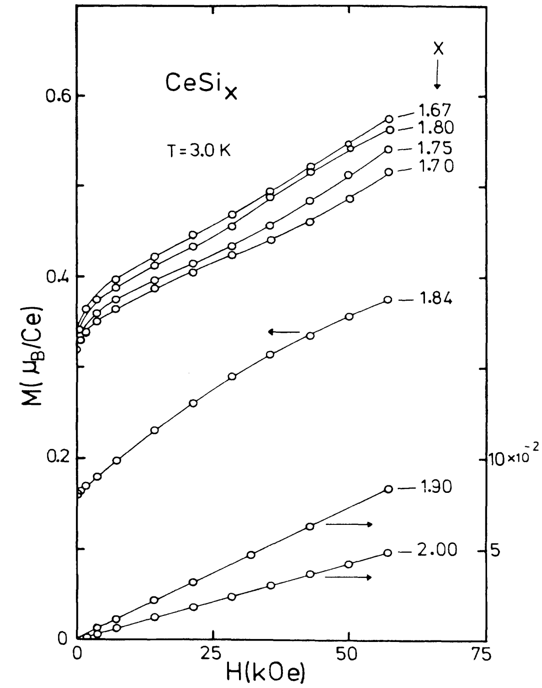

FIG. 3. Field dependence of the magnetization of as-cast CeSi$_x$ at 3.0 K. Solid lines are guide to eye. Units for the scale on right are $\mu\beta$/Ce.

agreement with previous results.[12] With decreasing x, the range of the Curie-Weiss behavior extended to lower temperatures. The effective paramagnetic moment (M_{eff}) and the Curie-Weiss parameter Θ for $CeSi_{2.0}$ (obtained from the susceptibility data above 200 K) are $2.74\mu_B$ and -249 K, respectively. Both M_{eff} and Θ decrease in magnitude with decreasing Si concentration x across the series (see Table I).

The magnetic-ordering temperatures were estimated using a low-field (360 Oe) static-susceptibility measurement[24] as well as by a nearly zero-field 87-Hz ac susceptibility measurement. No magnetic or superconducting ordering was observed in $CeSi_{1.9}$ and $CeSi_{2.0}$ down to 400 mK. Magnetic-ordering-temperature data for other samples are given in Table I.

At 300 K the magnetization (M) has a linear field dependence for all CeSi$_x$ samples. The M versus H behavior at 3.0 K is depicted in Fig. 3. The M versus H curve at 3.0 K is linear for $CeSi_{1.9}$ and $CeSi_{2.0}$ which do not order magnetically. For magnetically ordered samples ($x \le 1.84$), the magnetic moment does not saturate even in fields up to 57 kOe. For samples with $x \le 1.80$, the magnetization shows a trend towards saturation in low fields (<35 kOe) and rises again for field values above 35 kOe. This behavior suggests that magnetic order in CeSi$_x$ samples may not be simple ferromagnetic. A spontaneous rise in the magnetic moment in a field value near 40 kOe has also been observed in recent measurements on a $CeSi_{1.7}$ single crystal.[25]

Magnetization and magnetic susceptibility data were also obtained on annealed samples. The magnetic susceptibility is essentially the same in as-cast and annealed state but magnetization data in the magnetically-ordered state (i.e., $x \le 1.84$ and $T < T_c$) differ slightly. The most probable cause for the observed difference would seem to be the magnetic anisotropy. Strong magnetic anisotropy has been recently observed in the measurements on single crystals of $CeSi_{1.7}$ and $CeSi_{1.86}$.[25]

The results of our magnetic measurements across the CeSi$_x$ series are in good agreement with those of Yashima *et al.*[16] and Ruggiero *et al.*[10] and for $CeSi_{2.0}$, also with those of Dijkman *et al.*[12] and Lawrence *et al.*[11] However, we do not observe a T^2 dependence in the low-temperature magnetic susceptibility as was reported by Yashima *et al.*[16] for $1.85 \le x \le 2.0$, nor is any Curie-Tail apparent in our low-temperature magnetic-susceptibility data (see Fig. 4) as Dijkman *et al.*[12] observed in their $CeSi_{2.0}$ sample. The magnetic-susceptibility data for $CeSi_{1.90}$ and $CeSi_{2.0}$ in Fig. 4 appear to follow a linear T dependence below 20 K. A comparison of the magnetic-susceptibility data of $CeSi_{1.9}$, $CeSi_2$, and $LaSi_{2.0}$ (which have been prepared from the starting materials of the

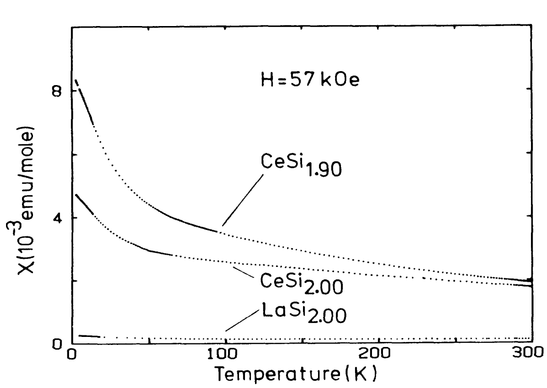

FIG. 4. Magnetic susceptibility of $CeSi_{1.9}$, $CeSi_{2.0}$, and $LaSi_{2.0}$ in a field of 57 kOe between 2.6 and 300 K.

same purity) shown in Fig. 4 would suggest that the "tails" in the magnetic susceptibility of $CeSi_{1.9}$ and $CeSi_{2.0}$ are not simply due to the presence of paramagnetic impurities but are an intrinsic property of the system.

In the magnetic regime for $x \leq 1.84$, Yashima *et al.*[16] had investigated only two samples, $CeSi_{1.7}$ and $CeSi_{1.8}$. Their values of the magnetic-ordering temperature agree well with our data in Fig. 5. In this regime the magnetic moments (both $M_{\rm eff}$ and M_s) are strongly reduced from the free-ion values and magnetic-nonmagnetic boundary would seem to be very sharp, since we find $CeSi_{1.84}$ to be magnetically ordered below 6 K, whereas Yashima *et al.*[16] have reported $CeSi_{1.85}$ to remain paramagnetic down to 100 mK.

ac susceptibility measurements and static magnetization measurements on $CeSi_{1.5}$ and $CeSi_{1.6}$ samples confirm the presence of antiferromagnetic $CeSi_{1.0}$ ($T_N = 5.6$ K) in the as-cast state and its absence in the annealed state, in agreement with the x-ray and metallographic results (see Fig. 6).

2. *High pressure*

High-pressure investigations across the $CeSi_x$ series were made on the annealed samples, $CeSi_{1.67}$, $CeSi_{1.80}$, and $CeSi_{1.84}$. Both the ordering temperature T_c and the saturation magnetic moment M_s (M_s in this case is taken as the value of M in 57 kOe at 3.0 K) show a linear pressure dependence for pressures up to 10 kbar, as seen in Fig. 7. It is evident in Fig. 8 that the pressure dependences of both T_c and M_s increases in a nonlinear fashion with increasing Si concentration. $\partial \ln T_c / \partial p$ and $\partial \ln M_s / \partial p$ attain their maximum values for $CeSi_{1.84}$ which is the sample closest to the magnetic-nonmagnetic boundary. The ordering temperature of $CeSi_{1.84}$ is reduced from 6.6 to 3.6 K under a pressure of 10 kbar. A

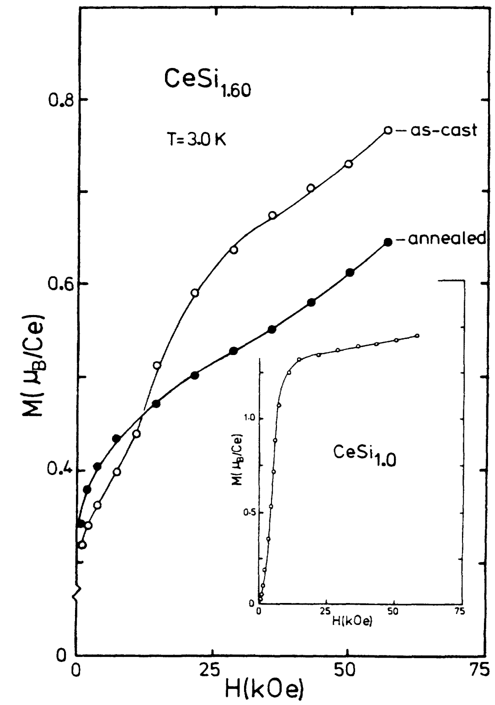

FIG. 6. Magnetic field dependence of the magnetization of $CeSi_{1.6}$ in the both as-cast and annealed states at 3.0 K. Presence of antiferromagnetic $CeSi_{1.0}$ in the as-cast state and its absence in the annealed state is evident from the magnetization curves. Insert shows field dependence of the magnetization of $CeSi_{1.0}$ at 3.0 K.

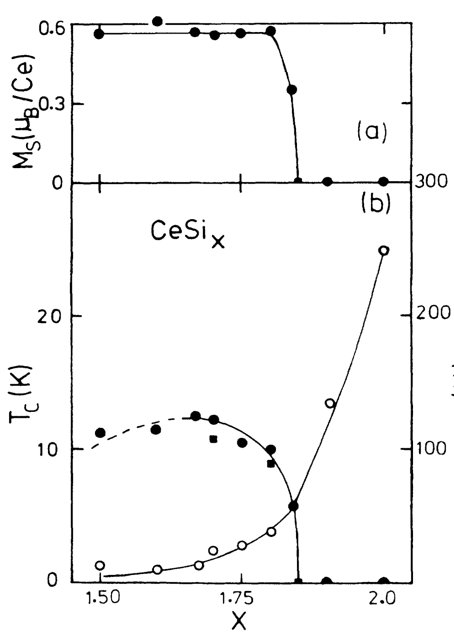

FIG. 5. Si-concentration dependence of the saturation magnetic moment M_s at 3.0 K in 57 kOe, the ordering temperature T_c, the negative of the Curie-Weiss parameter ($-\Theta$) across the $CeSi_x$ series. (■) shows data of Yashima *et al.* from Ref. 16; (○) and (●) are the present results. Solid lines are guide to eye. Dashed lines indicate data from multiphased samples.

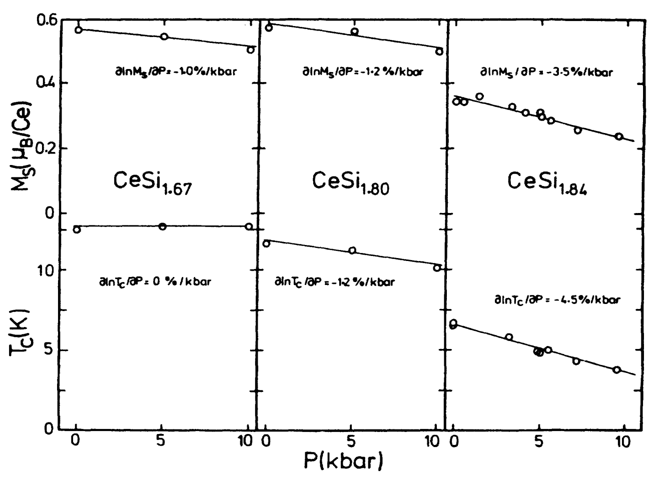

FIG. 7. Pressure dependence of the saturation magnetic moment at 3.0 K and the ordering temperature of $CeSi_x$ samples. Solid lines give least-squares fit to the data.

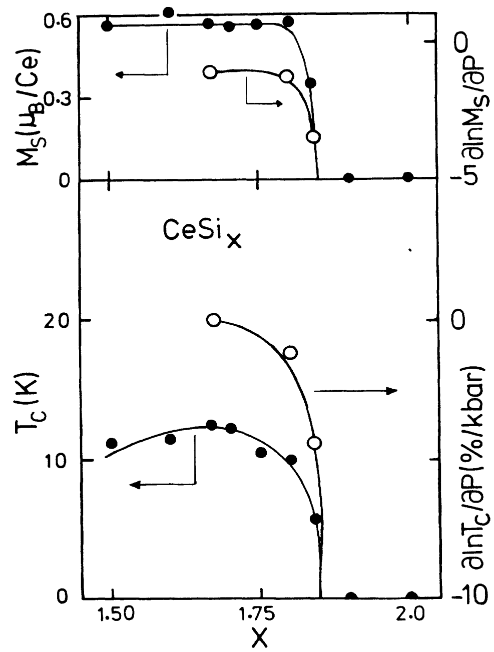

FIG. 8. Magnetic-ordering temperature T_c, saturation magnetic moment M_s, and their pressure dependences as function of Si concentration x across the $CeSi_x$ series. Logarithmic pressure derivatives of both T_c and M_s are in units of %/kbar.

linear interpolation suggests that a pressure of ~ 20 kbar would be sufficient for the complete destruction of the magnetism of this sample.

In Fig. 8, we compare the $M_s(x)$ and $T_c(x)$ behavior with the $M_s(p)$ and $T_c(p)$ behavior. It is apparent that both increasing pressure and increasing Si concentration (x) lead to the reduction in the magnetic moment and the ordering temperature in a similar nonlinear fashion. This observation indicates a qualitative similarity of the $|J(x)|$ and $|J(p)|$ behavior in this system.

Here it may seem strange that, in spite of the qualitative similarity of $|J(x)|$ and $|J(p)|$, instead of a volume reduction (which is always the case under pressure) an increase in the unit cell volume is observed as x is increased in $CeSi_x$ (see Fig. 1). It thus appears that the increase in the valence-electron charge with x leads to an increase in the hybridization with Ce's $4f$ state which dominates over the effect from the unit-cell expansion.

IV. DISCUSSION

Before discussing the physics of the $CeSi_x$ system in its homogeneous single-phase regime ($1.67 \leq x \leq 2.0$), we make a remark regarding the physics of its multiphase regime (< 1.67). An interesting feature of the present study is the detection of a stable Ce-Si phase. In the latest Ce-Si phase diagram no stable phase has been shown to exist with composition intermediate to $CeSi_{1.0}$ and Ce_3Si_5.[26] Our x-ray and metallographic data clearly indicate the presence of a stable phase in this concentration range. This phase, which appeared only on annealing $CeSi_{1.5}$ and $CeSi_{1.6}$ samples, may be forming peritactically.

The physics of $CeSi_x$ in its homogeneous regime ($1.67 < x < 2.0$) is quite complex. In this regime, there is evidence for a structural transformation, which brings in additional complications. The observed M versus H behavior at 3.0 K indicates a possible complex spin alignment. Electric crystal-field effects and many-body (Kondo) effects may also contribute to the complex magnetic behavior of this system.

The observed structural transformation in $CeSi_x$ system which apparently occurs in the same Si-concentration range ($1.84 < x < 1.9$) where magnetic nonmagnetic phase boundary occurs and specific-heat coefficient γ diverges can, in principle, effect both magnetic and specific-heat behavior. However, it is not possible to predict the importance of this effect. Therefore, the question of whether or not the structural transformation is responsible for the diverging nature of γ and sharp magnetic-nonmagnetic boundary in $CeSi_x$ remains open. Low-temperature x-ray work (in progress)[27] may provide some further information in this regard. In the following we assume that the structural transformation has a negligible influence on the magnetic properties.

Since the observed ground-state magnetic moments are much reduced below the theoretical values ($2.14\mu_B$ for Ce^{3+} free ion and $0.71-1.0\mu_B$ for Γ_7 ground state in a tetragonal symmetry) the magnetism of $CeSi_x$ cannot be explained by the simple RKKY-mechanism alone, even if electric crystal-field effects are taken into consideration. Complex magnetic spin structure alone can perhaps account for the reduced ground-state magnetic moments but it would not explain the reduction in the effective paramagnetic moment. In the following we invoke the many-body (Kondo) effect in an attempt to account for the behavior of this complex but interesting system.

We have discussed the basic mechanism behind the Kondo-lattice phenomena in the Introduction. A quantitative picture of the Kondo lattice was first given by Doniach[7] who proposed the schematic $T_c - J$ diagram seen in Fig. 9. In this model the magnetic-ordering tem-

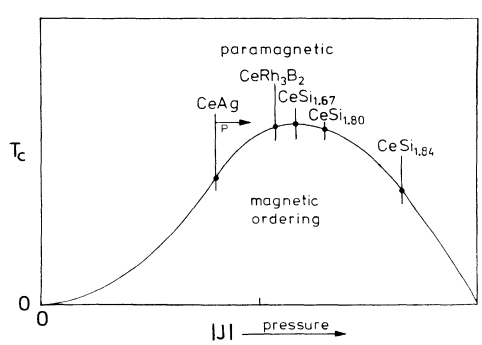

FIG. 9. Magnetic phase diagram of a Kondo lattice from Ref. 27. The position of $CeSi_x$, CeAg, and $CeRh_3B_2$ on the bell-shaped curve is made on the basis of the behavior of T_c and M_s under high-pressure conditions.

perature T_c increases initially as J^2; however, as $|J|$ is increased further, a critical value is reached where Kondo fluctuations begin to weaken the magnetism. This reduces both the magnetic moment and the ordering temperature and finally they fall to zero. T_c as a function of $|J|$ thus resembles a bell-shaped curve shown in Fig. 9. A similar phase diagram for a Kondo lattice was also presented by Lacroix *et al.*[8]

The $T_c(x)$ behavior of $CeSi_x$ shown in Fig. 5 is Kondo-lattice-like if a direct relation between x and $|J|$ is assumed. $|J|$ is related to the hybridization width Δ of the $4f$ level and excitation energy E_{ex} by the expression $|J| = [\Delta/N(0)|E_{ex}|]$.[28] An increase in Si concentration x in $CeSi_x$ would increase the component of hybridization between Ce $4f$ and Si $3sp$ states and hence the hybridization width Δ. An increase in x may also change E_{ex}, however, x-ray photoemission studies on $CeAl_2$ (whether or not it is alloyed with Y and Sc)[29,30] and on the chalcogenides and pnictides of Ce (Ref. 31) show that the chemical or external pressure mainly influence the hybridization width rather than the excitation energy. Therefore, in our case we ignore the changes in E_{ex} for simplicity, and the assumption of a direct relation between x and $|J|$ can be justified. Further support for this assumption comes from the qualitative similarity of the $|J(x)|$ and $|J(p)|$ dependences as seen in Fig. 8. In Ce systems it has been demonstrated that $|J|$ increases under pressure.[32] Therefore, in the $CeSi_x$ $|J|$ can be made to increase either by increasing the pressure or by increasing the Si concentration x.

The evidence for Kondo-lattice-like behavior in $CeSi_x$ is further strengthened by the high-pressure results. Within this model one would expect a slow $T_c(|J|)$ dependence when T_c is near its maximum value and a strong $T_c(|J|)$ dependence near the magnetic-nonmagnetic boundary. We observe very slow $M_s(p)$ and $T_c(p)$ dependence for $CeSi_{1.67}$ sample which has the highest T_c value among the series; these pressure dependences increase with increasing Si concentration and take on their maximum values for $CeSi_{1.84}$ which lies at the magnetic-nonmagnetic boundary. $CeSi_x$ is among the few ferromagnetic systems which exhibit Kondo-lattice-like behavior. The first example of a Kondo-lattice behavior in a ferromagnetic Ce system was reported by Eiling and Schilling[33] in CeAg under high-pressure conditions. Kondo-lattice-like behavior in ferromagnetic $CeRh_3B_2$ (Ref. 34) and $CePt_xNi_{1-x}$ (Ref. 35) has also been reported recently. We allocate the position of the ferromagnetic Ce systems on the Kondo-lattice curve in Fig. 9, in view of their behavior under high pressure. The ordering temperature of CeAg increases initially, passes through a maximum, and then falls off as pressure is increased; therefore, it is positioned on the left of the bell-shaped Kondo-lattice curve. $CeSi_{1.67}$ and $CeRh_3B_2$ both have high values of the ordering temperatures and their T_c's respond to the pressure only very slowly, so they are at the top of the hill. $CeSi_{1.8}$ and $CeSi_{1.84}$ show a decrease in T_c under pressure and, therefore, are placed on the right portion of the curve.

A point which is of basic importance and has not yet been seriously considered is that Kondo-lattice models predict an antiferromagnetic ground state in all cases. Experiments on above mentioned systems, however, indicate a Kondo-lattice-like behavior in spite of their ferromagnetic ground state. This provides a task for theoreticians to explore the possibility of a ferromagnetic Kondo-lattice state.

Another aspect of Ce systems which is currently being debated[36] is the significance of both Ce $4f$-Ce $4f$ wave functions overlap (in the spirit of the Hill limit[37]) and Ce $4f$ and ligand orbital hybridization in the delocalization process of Ce moment. In this context, the situation for $CeSi_x$ is quite clear as the Ce-Ce separation 4.66 Å is far above the Hill limit 3.4 Å. In $CeSi_x$, therefore, the question of $4f$-$4f$ overlap does not arise and the delocalization of the Ce moment follows via Ce $4f$-Si $3sp$ orbital hybridization.

V. CONCLUSIONS

In this paper it has been shown that the homogeneity of the $CeSi_x$ phase is limited to the Si concentrations: $1.67 \le x \le 2.0$ and is not extended to $1.55 \le x \le 2.0$, as was reported earlier.[16,17] The detection of an unknown stable phase with composition somewhere between $CeSi_{1.0}$ and Ce_3Si_5 indicates that phase diagram of Ce-Si system is more complicated than that reported by Gschneider and Verkade.[26] The magnetic structure is probably not simple ferromagnetic in $CeSi_x$; its magnetic properties appear to be Kondo-lattice-like both at ambient and high pressure. As regards possible heavy-fermion behavior in this system the situation remains speculative, since the importance of the effect of the tetragonal/orthorhombic transformation on the magnetic and specific-heat properties is quite uncertain.

Note added to the proof. The results of the low-temperature x-ray studies, which were referred in the text as in progress (Ref. 27), does not support the interpretation of the diffuse splitting of (200) line for Si concentration $x \ge 1.80$ for the initiation of the orthorhombic transformation. Therefore, the ambiguity regarding the possibility of a heavy-fermion behavior in $CeSi_x$ is clarified. The results of the high-pressure magnetization measurements discussed in this paper are fully consistent with the possibility of heavy-fermion behavior, and in fact, speak for heavy-fermion behavior for $1.8 < x < 1.9$ in this system. We discuss this aspect together with the low-temperature x-ray results elsewhere.

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